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Positron Annihilation Spectroscopy and Small Angle Neutron Scattering Characterization of Nanostructural Features in Irradiated Fe-Cu-Mn Alloys

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ABSTRACT

Radiation embrittlement of nuclear reactor pressure vessel steels results from a high number density of nanometer sized Cu-Mn-Ni rich precipitates (CRPs) and sub-nanometer matrix features, thought to be vacancy-solute cluster complexes (VSC). However, questions exist regarding both the composition of the precipitates and the defect character and composition of the matrix features. We present results of positron annihilation spectroscopy (PAS) and small angle neutron scattering (SANS) characterization of irradiated and thermally aged Fe-Cu and Fe-Cu-Mn alloys. These complementary techniques provide insight into the composition and character of both types of nanoscale features. The SANS measurements indicate populations of CRPs and VSCs in both alloys. The CRPs are coarser in the Fe-Cu alloy and the number densities of CRP and VSC increase with the addition of Mn. The PAS involved measuring both the positron lifetimes and the Doppler broadened annihilation spectra in the high momentum region to provide elemental sensitivity at the annihilation site. The spectra in Fe-Cu-Mn specimens thermally aged to peak hardness at 450°C and irradiated at 288°C are nearly identical to elemental Cu. Positron lifetime and spectrum measurements in Fe-Cu specimens irradiated at 288°C clearly show the existence of long lifetime (~500 ps) open volume defects, which also contain Cu. Thus the SANS and PAS provide a self-consistent picture of nanostructures composed of CRPs and VSCs and tend to discount high Fe concentrations in the CRPs.

INTRODUCTION

Reactor pressure vessel (RPV) embrittlement results from hardening caused by a high number density of ultra-fine scale features formed during irradiation. A combination of theory [1,2] and experimental techniques, including extensive three-dimensional atom probe (3DAP) [3-5] and small angle neutron scattering (SANS) [6-9] characterization, has established that nanometer sized Cu-Mn-Ni precipitates (CRPs), or clusters, are often the dominant embrittling feature in Cu bearing steels. A secondary embrittling feature, relatively independent of Cu, accumulates with neutron dose and produces significant embrittlement at high fluence, even in low Cu steels [10]. The latter have been termed stable matrix features (SMFs) based on their post-irradiation annealing recovery kinetics [2,8]. Theory and atomistic simulations, as well as the annealing experiments, suggest that the SMFs are three dimensional, sub-nanometer vacancy-solute (Mn, Cu and Ni) cluster complexes (VSCs) that initially form in displacement cascades [2,9,11]. The balance of CRPs and VSCs depends on the combination of metallurgical and irradiation variables [2,11].

However, there is a significant controversy regarding the actual CRP composition [3-5,9,12] and up until now, the vacancy character of the SMFs has largely rested on interpretations of annealing signatures and simulation results [2,8,9,11]. While the 3DAP and SANS measurements generally reveal similar CRP-type feature number densities, sizes and Mn and Ni contents that are consistent with both SANS (see below) and theoretical predictions, they give very different views of their composition. The 3DAP results have been interpreted to suggest that the nanoscale solute clusters are Cu enriched, but contain significant quantities of Fe (> 50%) [3-

5]. In contrast, standard interpretation of a large body of SANS data, including on alloys with systematic variations in the key elements indicate the presence of well-formed CRPs that contain Cu (typically ~70%), Ni and Mn, but little or no Fe [6-9]. There are also alternative candidates for SMFs, including interstitial cluster complexes, dilute atmospheres of solutes and other nanoscale phases associated with wide variety of elements [2,4,11].

Both SANS and 3DAP have significant limitations. In principle, 3DAP offers the potential of near atomic resolution. However, the resolution is not absolute and is influenced by trajectory aberrations associated with the complex topology of the evaporation surface at CRPs and SMFs like VSC [5]. Due to the very small size of these features, positional uncertainties of 0.5 nm or less would artificially place significant numbers of iron atoms in a CRP and solute atoms in the adjoining iron matrix. The 3DAP technique also suffers from limited statistics associated with sampling very small material volumes, cannot detect defects or defect clusters and may experience preferential pre-evaporation of solute atoms. While SANS measurements sample much larger material volumes, the data analysis relies on assumptions, particularly regarding the magnetization of CRPs and SMFs, and suffers co-variance and non-uniqueness associated with de-convoluting the scattering contributions from multiple, size distributed scattering features.

The objective of this work is to use the combination of PAS and SANS to partly mitigate their individual limitations in characterizing the nanostructural features formed in irradiated Fe-Cu and Fe-Cu-Mn alloys. The SANS technique provides information on the CRP size, number density and volume fractions, as well as providing insight on their compositions. The PAS technique is unique in its ability to detect the presence of vacancy and vacancy cluster trapping centers and most recently, the chemical composition of the trapping site as well. Further, positrons are also ‘trapped’ in Cu precipitates¹. By combining PAS and SANS and other techniques, the potential exists to both help identify the basic defect character of the SMFs and to help resolve the discrepancy between the SANS and 3DAP views of precipitate composition.

EXPERIMENT

Binary Fe-0.9wt% Cu and ternary Fe-0.9 wt% Cu-1.0 wt% Mn alloys were solution annealed at 775°C for 17 hours followed by a 3-minute salt quench to 450°C prior to air-cooling. This heat treatment was intended to keep the Cu in supersaturated solution prior to irradiation or thermal annealing. Coupons of these alloys approximately 1 cm x 1 cm x 2 mm thick were thermally aged at 450°C for 24 hours and neutron irradiated at 288°C in a flux of about 7×10^{15} n/m²-s to a fluence of 0.9×10^{23} n/m².

The SANS experiments were performed at the National Institute of Science and Technology (NIST) Center for Neutron Research [14]. Small angle neutron scattering arises from both nuclear (N) and magnetic (M) scattering length density differences between the ferrite matrix and the scattering feature. Thus the samples were measured in a strong magnetic field (~1.7T) that saturated the iron matrix. The scattering from a well-collimated beam of 0.5 nm wavelength neutrons was recorded on a position sensitive detector with a maximum q-range of about 3 nm⁻¹. The scattering data for the radiation induced features were calculated by subtracting background counts, parasitic scattering and normalized scattering from an unirradiated control specimen from the net scattering count recorded in each detector pixel. The corrected data were then converted to absolute scattering cross-sections, $d\Sigma/d\Omega$, by normalizing

¹ The physical mechanism responsible for positron confinement in CRPs is different than in the case of vacancy defects. Positron localization in CRPs results from the strong positron affinity of copper (-4.81 eV) relative to iron (-3.84 eV) [13], while vacancy trapping is due to missing ionic core(s) and a decreased electron density associated with an open volume defect.

to a water reference sample, including standard accounting for transmission and sample volumes. The cross section data were then averaged over small increments of q and the angle ϕ with respect to the magnetic field direction.

The magnetic component of the $d\Sigma/d\Omega(q,\phi)$ data were analyzed by least-squares fits assuming log-normal size distribution(s) of spherical scattering features. The features were assumed to act as magnetic holes in a saturated ferromagnetic iron matrix. Since the magnetic scattering contrast is precisely known, this assumption provides absolute estimates of the number density and volume fraction of the scattering features. The magnetic to nuclear (M/N) scattering ratio provides information about the composition of the scattering feature(s). In the case of simple binary and ternary Fe-Cu-Mn alloys, the M/N ratio provides a relatively clear indication of precipitate composition. Additional details regarding the SANS experiments and analysis are provided elsewhere [8,9].

The PAS measurements were performed using the Lawrence Livermore National Laboratory (LLNL) Pelletron facility. The Pelletron is a 3.0 MeV electrostatic accelerator that forms a positron beam with a flux of $\sim 6.5 \times 10^9$ e⁺/m²-s from a 70 mCi ²²Na source. The use of a high-energy positron beam allows the characterization of bulk specimens, which do not need to be mounted in vacuum and improves the signal to noise ratio by eliminating background radiation from the positron source. The experimental setup and methods to evaluate and deconvolute positron lifetime spectra and measure and interpret Doppler broadened annihilation spectra are described in more detail elsewhere [15,16].

Briefly, thermalized positrons experience a repulsive potential from ionic cores and attractive potential from electrons and open volume defects. Thus vacancy features and regions with strong positron affinity, including nanovoids (VSCs) and CRPs, effectively 'trap' the positrons. Hasegawa and co-workers have shown that nearly all positrons localize and annihilate in a quantum dot type structure of nanoscale pure Cu precipitates formed in a thermally aged Fe-1.0%Cu alloy [17]. Positron annihilation with electrons produces predominately two gamma rays, which are shifted up or down in energy (Doppler shifts) around 0.511 MeV by an amount $\Delta E = 1/2p_{LC}$, where p_L is the longitudinal component of the electron-positron momentum in the direction of gamma ray emission [16]. The ΔE can be precisely determined with good signal to noise ratio using a coincidence, two detector setup. Annihilation with more localized 3d transition metal electrons produce Doppler shifts that extend into the high momentum region. In contrast, annihilation with more spatially extended valence electrons in nanovoids makes a negligible contribution to ΔE at high momentum. The exact shape of the ΔE curves depends on the characteristics of the 3d electrons, hence on the atomic species at the annihilation site. Thus, analysis of the high momentum region of the Doppler broadened curve can be used to determine the elemental composition of the trapping feature.

RESULTS

Thermally aged alloys

SANS and PAS characterization of the Fe-Cu and Fe-Cu-Mn alloy following thermal aging at 450 °C for 24 hours indicate the presence of a high number density of nearly pure, defect free Cu precipitates. The SANS scattering cross-sections fit to a single, log-normal size distribution and resulted in mean radii, number densities and volume fractions of 0.9 and 1.3 nm, 9×10^{23} and 5×10^{23} m⁻³ and 0.23 and 0.49% for the Fe-Cu and Fe-Cu-Mn alloy, respectively. The measured magnetic to nuclear scattering ratio of 9.6 for the Fe-Cu alloy is close to, but actually slightly higher than the value typically associated with a pure Cu precipitate (~ 7.6) [12]. This could be due to the presence of a small amount of Fe ($\sim 10\%$). The value of 5.3 for the Fe-Cu-Mn alloy is consistent with precipitates containing about 96% Cu and 4% Mn.

A slight increase in the mean positron lifetime value was obtained for both thermally aged alloys from 109 ps (as-received control) to 114 ps (Fe-Cu) and from 110 to 114 ps (Fe-Cu-Mn). Figure 1a and 1b show the normalized (to the as-received control) Doppler broadened spectra for the Fe-Cu and Fe-Cu-Mn alloy, respectively. These Figures also show a reference spectrum for pure, well-annealed elemental Cu. The thermally aged spectra from both the Fe-Cu and Fe-Cu-Mn alloys are nearly identical to that of pure Cu, indicating that the positrons are localized within nearly pure Cu precipitates, consistent with the results of Hasegawa et al [17]. Note the slightly lower ratio in the high momentum region of the Fe-Cu-Mn alloy is consistent with a small amount of Mn in the precipitates. The calculated positron lifetime of bcc Cu is 110 ps, only slightly longer than the value of 107 ps calculated for both fcc Cu and bcc Fe. Thus, the slight increase in the mean positron lifetime with thermal aging is also consistent with pure Cu, vacancy free precipitates.

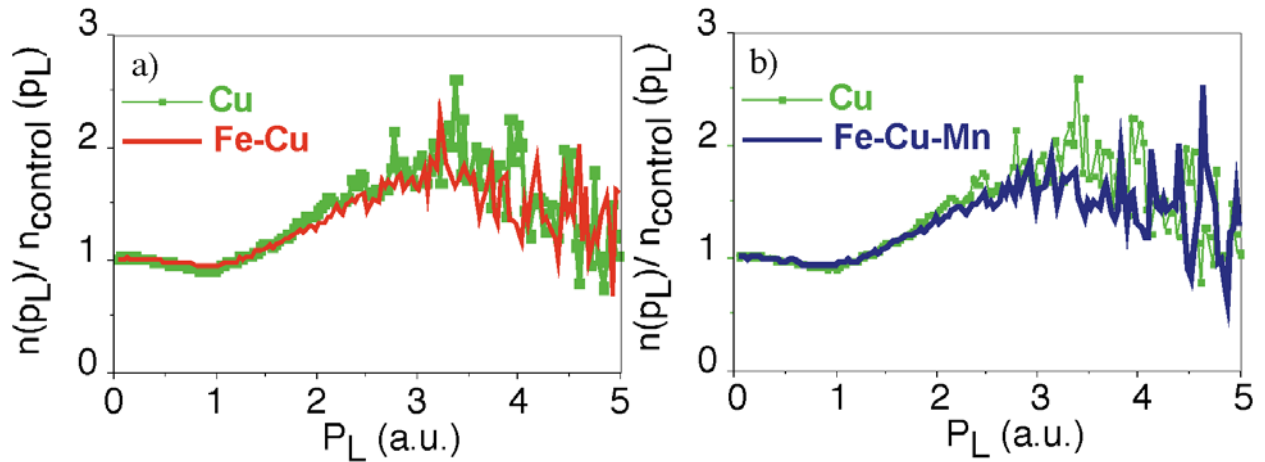


Figure 1 – Normalized Doppler-broadened spectra for 450°C, 24 hour thermally aged for a) Fe-0.9 wt% Cu and b) Fe-0.9 wt% Cu-1.0 wt% Mn alloy. Both spectra are nearly identical to elemental Cu (shown in green) and significantly different than Fe, which would correspond to a uniform value of 1.

Neutron irradiated alloys

The neutron irradiated SANS scattering cross-sections of both the Fe-Cu and Fe-Cu-Mn alloys are inconsistent with the presence of only one scattering feature to a high level of statistical confidence. However, two-feature (labeled 1 and 2), log-normal size distributions provide excellent fits to the data in both cases. For the Fe-Cu alloy, the two-feature fit results in mean radii of 3.4 and 0.9 nm, number densities of $4.6 \times 10^{22} / \text{m}^3$ and $1.2 \times 10^{23} / \text{m}^3$, volume fractions of 0.75 and 0.04% and M/N ratios of 6.7 and 1.5 for feature 1 and 2, respectively. The M/N for feature 1 is consistent with nearly pure Cu precipitates with less than 3% vacancies and that for feature 2 is consistent with a small VSC containing about 60% copper and 40% vacancies. For the Fe-Cu-Mn alloy, the two-feature fit results in estimates of mean radii of 2.0 and 1.0 nm, number densities of $2.3 \times 10^{23} / \text{m}^3$ and $3.0 \times 10^{23} / \text{m}^3$, volume fractions of 0.78 and 0.11% and M/N ratios of 4.6 and 2.0 for feature 1 and 2, respectively. In this case, feature 1 is consistent with CRPs that contain about 6% Mn and 94% Cu, while feature 2 is consistent with a population of VSCs including Mn, with about 70% Cu. Both the VSC and CRP number densities are higher in the Fe-Cu-Mn alloy. The CRPs are smaller in this case while the VSCs are similar in size to those found in the Fe-Cu alloy. It is important to note that the precise numerical parameters derived from the two-feature fits are not unique and are somewhat to strongly co-variant particularly when the sizes of the two features are more similar. However, the exact

number densities and volume fractions aside, the interpretation that there are multiple features with different M/N ratios is very robust and provides important insight on the nanofeatures that form under irradiation.

The positron lifetime analysis revealed a significant increase in the mean lifetime from 109 to 233 ps for the Fe-Cu alloy, while the Fe-Cu-Mn alloy showed a much more modest increase from 110 to 122 ps. The positron lifetime fitting procedure yielded three distinct lifetime components for the Fe-Cu alloy. The two longer lifetime components, with lifetimes and intensities of 227.8 ps/42.5% and 520 ps/19.3% are interpreted as positrons trapping in vacancy-type defects. Calculations indicate that a positron lifetime of 520 ps would be consistent with a 3-dimensional vacancy cluster containing 50 or more vacancies and a radius of 0.5 nm or larger. To the best of our knowledge, this represents the first measurement of such a significant population of long-lifetime component (large vacancy clusters) in Fe-based steels or alloys irradiated at 288°C.

Figure 2a and 2b show the normalized Doppler broadened spectra for the Fe-Cu and Fe-Cu-Mn alloy, respectively, along with the reference spectrum for elemental Cu. In contrast to the thermally aged case, the Doppler broadened spectrum in the irradiated Fe-Cu alloy is not identical to elemental Cu, but actually has a peak at low momentum [$p_L < 1$ atomic unit (a.u.)] values and shows a slight peak, indicative of Cu at higher ($p_L > \sim 2.5$ a.u.) values. Consistent with the positron lifetime measurements, these coupled observations suggest significant positron trapping at vacancy-Cu cluster complexes. The Doppler broadened spectrum of the irradiated Fe-Cu-Mn alloy is again nearly identical to that of pure Cu, although the intensity is slightly lower than the thermally aged specimen. This small difference might suggest the presence of some Mn or Fe in the CRPs. Note higher Mn enrichment is consistent with both the thermodynamic effect of the lower irradiation temperature compared to the thermally aged samples and the SANS magnetic to nuclear scattering ratio results. Overall, however, the momentum spectrum in the Fe-Cu-Mn alloy indicates that the CRPs are highly enriched in Cu. The differences between the Fe-Cu and Fe-Cu-Mn alloys might be attributed to the effect of sink competition between VSCs and CRPs. In the case of the Fe-Cu alloys the lower number density of CRPs allows positrons to find the higher concentration of VSC traps. However, in the Fe-Cu-Mn alloy, the CRP and VSC densities are comparable and annihilation takes place primarily in the CRPs.

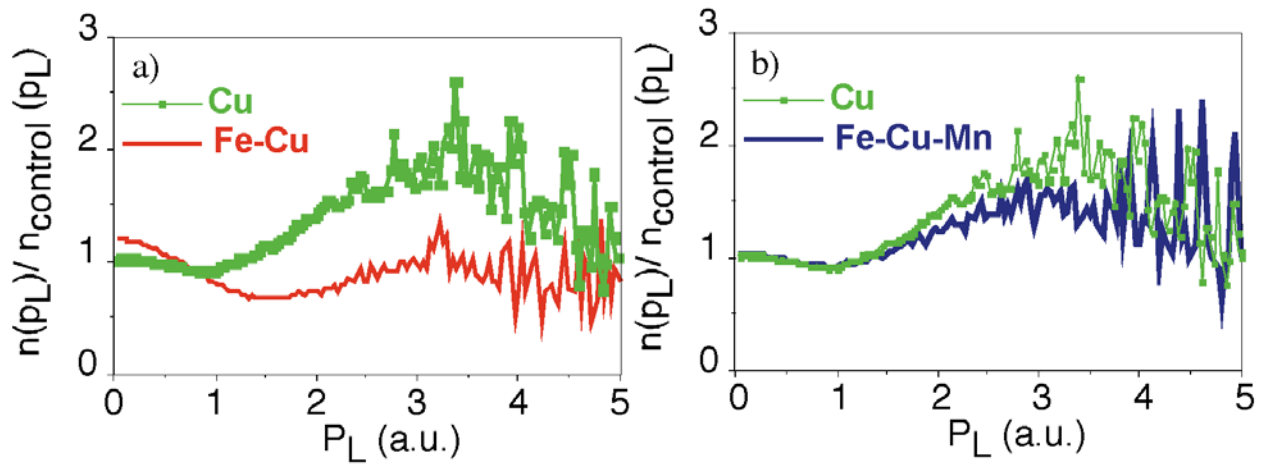


Figure 2 – Normalized Doppler-broadened spectra for 288°C neutron irradiated a) Fe-0.9 wt% Cu and b) Fe-0.9 wt% Cu-1.0 wt% Mn alloy.

CONCLUSIONS

A complementary PAS and SANS characterization of thermally aged and neutron irradiated Fe-Cu and Fe-Cu-Mn alloys is reported. For thermally aged alloys, both the SANS and PAS indicate the presence of a high number density of nearly pure, defect free Cu precipitates. The SANS and PAS results of the 288°C neutron irradiated Fe-Cu alloy reveal a smaller number density of large ($r \sim 3.4$ nm) CRPs and the presence of smaller vacancy-Cu cluster complexes (VSCs), which are the dominant positron trap. Notably, this is the first positron lifetime identification of large vacancy clusters in Fe-based alloys neutron irradiated at near 288°C. Similar measurements on the neutron irradiated Fe-Cu-Mn alloy revealed the presence of CRPs with a nearly identical Doppler broadened spectrum to that of both the thermally aged alloy and elemental Cu. This suggests that the precipitates do not contain a significant amount of Fe. Further, trapping at large vacancy complexes is not observed in the irradiated Fe-Cu-Mn alloy. This may be due to either a dominance of precipitate trapping relative to any vacancy-solute (Cu-Mn) complexes present in this case, or to the suppression of the formation of larger vacancy clusters by the Mn. Of course both effects may occur in combination. Future work will focus on further clarifying these issues.

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